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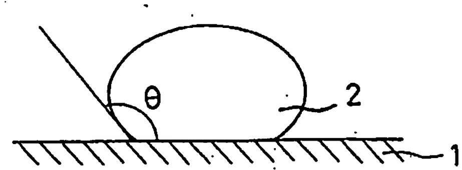
(54) **Tread rubber composition and tyre using the composition.**

(57) A tread rubber composition of excellent hydrophobic property and water repellency suitable to a studless tyre of excellent performance on ice, comprising a diene rubber comprising at least one rubber selected from the group consisting of natural rubber, isoprene and polybutadiene as a main ingredient and, based on 100 parts by weight of the diene rubber, from 10 to 40 parts by weight of a clay comprising kaolinite as a main ingredient and having an oil absorption amount of from 50 to 70g/100g and 0.1 to 8 parts by weight of a silane coupling agent.

FIG. 1



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The present invention concerns a tread rubber composition having excellent performance on ice and suitable for a studless tyre, as well as a tyre having a tread manufactured using the rubber composition.

A spiked tyre exhibits an excellent gripping force on a frozen road surface. Since the spiked tyre has a large digging friction force, among hysteresis loss friction, adhesion friction and digging friction which are the factors mainly related to the gripping force between a tread rubber and a road surface, it exhibits an excellent gripping force on a frozen road surface.

However, use of the spiked tyre has gradually been restricted legally as a countermeasure for public pollution caused by powdery dusts in recent years, and a studless tyre with no spikes have been rapidly popularised. In some studless tyres, the digging friction force is improved, for example, by the device of incorporating a blowing agent or organic fibres thereby increasing the unevenness on the surface of the tread. However, since a studless tyre has a lower digging friction force compared with a spiked tyre, its gripping force is inferior. In particular, if the road surface is ground flat by slip or idle rotation of a tyre upon starting on a frozen road surface, the gripping force of the studless tyre is even more deteriorated and so further improvement is now demanded.

On a road surface with an extremely low friction coefficient such as a frozen road surface, the hysteresis loss friction is extremely small but adhesion friction (tract) also contributes to the improvement of the gripping force in addition to the digging friction. Therefore, it has been arranged to increase the gripping force on the frozen road surface for a studless tyre by increasing the one other of the frictions contributing to the gripping force, that is, the tract.

As a method of improving tract it has been proposed to eliminate hydroplaning caused upon thawing of the frozen road surface caused by friction upon starting and braking, thereby increasing the area of contact between the tread rubber and the iced surface, or by making the rubber material softer to increase the area of contact with the road surface.

Increased unevenness on the tread surface can increase the digging friction, as well as taking up surface water into concave portions to eliminate hydroplaning. However, increase of the concave portions for the elimination of the hydroplaning effect leads to decrease in the area which is in contact with the iced surface, which is contrary to the required improvement of the gripping force based on an increase in the area of contact, so that the effect is limited.

On the other hand, US Patent No 4 522 970 discloses a tread composition incorporation kaolinite clay and 3,3'-bis(trimethoxysilyl propyl)polysulfide in a certain rubber ingredient can improve wet skid resistance. However, tread rubbers for use in a studless tyre in disclosed examples have an insufficient performance on ice. In addition, the blending with the clay generally deteriorates the reinforcing performance of the rubber and the rubber ingredient (butadiene and SBR) used for the tyre and in the disclosed examples there is seen a large amount of wear, which is thus not suitable to a tread rubber.

An object of the invention is to provide a tread rubber composition based on a diene rubber ingredient used customarily, and capable of improving the performance on ice causing no problem in the reinforcing performance of the tread rubber, by improving the tract force by the elimination of hydroplaning and increase in the area of contact with a road surface.

The present inventors, et al, discovered a rubber composition of excellent hydrophobic property and water repellent property, which allows an increase in the area of contact between a tyre and a road surface by reducing water-deposition on the surface of the tread and have thus accomplished the present invention.

According to the present invention therefore a tread rubber composition comprises a diene rubber comprising at least one rubber selected from the group consisting of natural rubber, polyisoprene and polybutadiene as a main ingredient and, based on 100 parts by weight of the diene rubber, characterised by 10 to 40 parts by weight of clay comprising kaolinite as a main ingredient and having an oil absorption amount of from 50 to 70g/100g and from 0.1 to 8 parts by weight of a silane coupling agent.

For a polymer, as a rubber ingredient in the tread rubber composition according to the present invention, a diene rubber having a low glass transition point (T_g) and less curing even at a low temperature, specifically, natural rubber, polyisoprene or polybutadiene is used so as to ensure a good area of contact even on a frozen road surface. The natural rubber, polyisoprene and polybutadiene may be used alone or in combination of two or more of them. If necessary, another diene polymer such as SBR may also be added.

In the tread rubber according to the present invention, a clay comprising kaolinite as a main ingredient and having an oil absorption amount of 50 to 70g/100g of the clay (hereinafter represented as an oil absorption amount of 50g/100g to 70g/100g) is blended, in order to eliminate hydroplaning between the tyre surface and the road surface. The oil absorption amount used herein means the amount of oil absorbed into the clay when the clay is immersed in the oil for a certain period of time, which is an indication representing the state of the structure. If the oil absorption amount of the clay is less than 50g/100g, the reinforcing performance is insufficient when it is applied to the tread, tending to cause chipping or early wearing of the tread. On the other

hand, if the oil absorption amount of the clay is more than 70g/100g, the size of clay coagulars is excessively small, in other words, the clay is in the form of a fine powder making it impossible for pelletisation and making handling difficult. Hard clay (oil absorption amount of about 20g/100g to 40g/100g) has generally been known as a clay to be blended with the tyre rubber composition. However, if such a hard clay is applied to a tread rubber for a studless tyre, it shows less improving effect for the performance on ice and snow and tends to cause insufficient reinforcing performance.

As stated above a reduction of the rubber reinforcing performance is not desirable since this causes deterioration of the wear resistance and deterioration of failure characteristics of the tyre tread.

Any clays capable of satisfying the foregoing requirements may be used in the present invention although clays sintered at 600°C to 800°C are preferred. Clays comprising kaolinite as the main ingredient sometimes have their hydrophilic groups exposed on the surface or contain structured water in crystals. Then, when they are sintered at 600°C to 800°C, they release the structured water to improve the hydrophilic property and contribute to the improvement of the water repellency of the tread rubber. Sintering at a temperature lower than 600°C makes it difficult to release the structured water in crystals and, on the other hand, sintering at a temperature higher than 800°C tends to change the crystal structure of kaolinite. For further improving the water repellency of the clay, it is preferred to treat the clay with the silane coupling agent after sintering.

The content of the clay is from 10 to 40 parts by weight, preferably from 10 to 30 parts by weight, based on 100 parts by weight of the rubber ingredient. If the blending amount of the clay is more than 40 parts by weight, the reinforcing performance is deteriorated particularly at a low temperature, which is not preferred. On the other hand, if the blending amount of the clay is less than 10 parts by weight, no substantial improvement in the present invention for the gripping force on the frozen road surface is obtained.

Since the reinforcing performance of the rubber composition generally tends to be deteriorated by the addition of the clay, it is preferred to further blend a reinforcing agent such as a carbon black or silica in the rubber composition for use in the tread according to the present invention. In this case, the content of the clay is preferably from 15 to 80% by weight based on the total amount of the content of the reinforcing agent such as carbon black (total amount of the reinforcing agent) and the blending amount of the clay. The total amount of the reinforcing agent is preferably from 50 to 90 parts by weight based on 100 parts by weight of the rubber ingredient.

In the tread rubber composition according to the present invention, it is preferred to add a silane coupling agent for further improving the water repellency. Silane coupling agents which can be used preferably are represented by the formula X_3SiR in which X represents an alkoxy group or a chlorine atom, R represents one of vinyl, glycide, methacryl, amino, mercapto, epoxy and imide groups, or represented by the formula:

$$(C_nH_{2n+1}O)_3\text{-}Si\text{-}(CH_2)_m\text{-}S_k\text{-}(CH_2)_m\text{-}Si(C_nH_{2n+1})O_2$$

in which n represents an integer of 1 to 4, and m and k each represents an integer of 1 to 6. Such a silane coupling agent forms a chemical bond with organic and inorganic materials in the rubber composition respectively to combine the organic and inorganic materials at the boundary. The blending amount of the silane coupling agent is from 0.1 to 8 parts by weight, preferably 0.1 to 5 parts by weight, based on 100 parts by weight of the rubber in the rubber composition. If it is less than 0.1 parts by weight, no substantial effect can be obtained, whereas if it is more than 8 parts by weight, material cost will be increased.

The silane coupling agent may be added separately to the composition, or it may be added as a clay treating agent. Addition as a clay treating agent is more effective. Namely, if the clay is previously treated with the silane coupling agent and then blended into the rubber composition, the hydrophobic property and the water repellency of the clay can act by way of the silane coupling agent, so that hydrophobic moieties can be converted into portions having the hydrophobic property in the rubber composition (not only the rubber ingredient but also the blending agents described later), to provide the tread rubber itself with the water repellency. When the tread rubber itself is provided with the water repellency, generation of water inclusions between ice and the tread rubber to the tread rubber can be suppressed and water droplets deposited on the surface of the tread rubber can be removed easily. As a result, a substantial area of contact between the tread rubber and the ice is maintained to increase the tract. That is, the gripping force on the iced road surface is improved.

The rubber composition according to the present invention may further contain, in addition to the compounds described above, other customary blending agents used in rubber industry such as vulcaniser, vulcanisation promoter, vulcanisation promotion aid, ageing inhibitor and softening agent. Further, in order to improve the hydroplane eliminating effect or digging friction to the road surface, organic fibres may be incorporated or a blowing agent may be added to cause blowing upon manufacture of the tyre.

As has been described above, in the tread rubber composition according to the present invention, since a predetermined amount of the clay having the oil absorption amount within a predetermined range is blended together with the silane coupling agent, it has the water repellency and the hydrophobic property with no substantial deterioration of the reinforcing performance. In particular, when the clay is previously treated with the

silane coupling agent and then blended, since the hydrophobic property of the tread rubber itself can be improved, it can contribute to the improvement of the area of contact with the iced road surface to increase the tract and shows excellent performance on ice. Further, when the clay sintered at about 600°C is used, it can exhibit the water repellency and the hydrophobic property effectively. Further, when the reinforcing agent such as carbon black is blended by a predetermined amount, deterioration of failure characteristics can be suppressed.

Accordingly, the tread rubber composition according to the present invention is most suitable for a tread rubber composition for use in a studless tyre to which a demand for the failure characteristics and wear resistance is not so severe but a demand for the braking performance on ice is severe. Then, the tyre having the tread manufactured by using the tread rubber composition according to the present invention has excellent performance on ice.

An embodiment of the present invention will now be described, by way of example only, in conjunction with the accompanying drawings:

Figure 1 is an explanatory view to show the angle of contact; and

Figure 2 is a view illustrating a system used for measuring the angle of contact.

The present invention will now be explained more specifically with reference to preferred embodiments.

Rubber compositions of Examples 1 to 5 and Comparative Examples 1 to 6 were prepared by blending polymers and various kinds of additives shown in Table 1 and further blending various kinds of blending agents (clay mainly composed of kaolinite, carbon black and silane coupling agent) each in the amounts shown in Table 2.

For the polybutadiene shown in Table 1, UBEPOLE BR 150L (trade name of products manufactured by Ube Industries Ltd.) was used. OZONON 6C (N-phenyl-N-(1,3-dimethylethyl)-p-phenylene diamine) manufactured by Seko Kagaku Co was used as the ageing inhibitor. NOCSELLER NS(N-tert-butyl-2-benzothiazyl sulfenamide) manufactured by Ohuchi Shinko Kagaku Co was used as the vulcanisation promoter.

For the carbon black shown in Table 2, SHOWBLACK N 220 manufactured by Showa Cabot Co was used. Three types of clays A, B and C were used as the clay. Both of clays A and B were amorphous meta-kaolin sintered at 600°C and had an oil absorption of 55g/100g. Clay C is referred to as a hard clay having an oil absorption amount of 40g/100g. Both clay B and clay C were treated with a silane coupling agent of vinyl-tri(t-methoxyethoxy) silane and contained 1% by weight of the silane coupling agent. In Example 6 and Comparative Example 2, Si69 manufactured by DEGUSSA Co was added as the silane coupling agent. Si69 is bis-triethoxysilylpropyl)tetra-sulfene. In the preparation of the rubber compositions, a process oil was blended by an amount shown in Table 2 to make the hardness of the compositions equal to each other in each of the Examples and Comparative Examples.

Vulcanised rubber test pieces were prepared by using the thus prepared rubber compositions, and the failure characteristics and the angle of contact with water were evaluated by the following methods. Further, studless tyres of 165R13 were manufactured by using the rubber compositions described above and the performance on ice of the tyres was evaluated by the following method. The results are shown together in Table. 2.

TABLE 1

	Blending amount (Parts by weight)
Natural rubber	70
Polybutadiene	30
Stearic acid	3
Zinc powder	3
Ageing inhibitor	1
Sulfur	1.5
Vulcanisation Promotor	0.5

Evaluation method

Failure Characteristics

Rubber tear strength was measured according to JIS K6301. Assuming the measured value as 100 for the tear strength of a rubber composition not containing clay and silane coupling agent (Comparative Example 1), measured values for the tear strength of other rubber compositions were represented each by an index. A small index value shows lower failure characteristics. Since the demand for failure characteristics on ice and snow road surface is not so severe as compared with that on a usual road surface, there is no practical problem in the tread for the studless tyre so long as the failure characteristics exceed about 80.

Performance on Ice

Studless tyres of size 165R13 (inflation pressure: 2kgf/cm^2 were manufactured using the rubber compositions described above and mounted on a 1500cc front wheel drive (FF) antilock braking system (ABS) car and measured under the following conditions:

Place of measurement	: Nayoro test course of Sumitomo Rubber Industries Limited (Iced surface road)
Atmospheric temperature	: -6.5°C
Ice temperature	: -4.0°C

For the measurement, the car was run at a speed of 30kg/h and then braked rapidly to determine the distance from the instance the wheels were locked till stopping of the car. Setting the stopping distance in Comparative Example 1 as 100, stopping distances measured for other Examples and Comparative Examples were indicated each by an index. As the index value is smaller, it shows better performance on ice.

Angle of Contact:

The angle of contact means the angle θ formed at the boundary at which rubber 1 and a water droplet 2 are in contact with each other where the droplet 2 is deposited to the surface of the rubber 1. This represents the wetability of water to rubber. If the angle of contact is larger, the tyre is less wetable and the water repellency of the rubber is better.

Using the system shown in Figure 2, the cosine of the angle of contact was measured for forward and backward movement to determine the angle of contact according to the following equation:

$$\theta = \cos^{-1}(1/2 \times (\cos\theta a + \cos\theta r))$$

in which θa is an angle of contact upon forwarding and θr represents an angle of contact upon backwarding.

Assuming the value for the angle θ n Comparative Example as 100, angles θ or other Examples and Comparative Examples were represented each by an index. As the index value is greater, the angle of contact is larger (more blunt angle).

TABLE 2

	Example					Comparative example					
	1	2	3	4	5	1	2	3	4	5	6
Process oil	0	4	8	12	6	0	0	2	16	8	4
Carbon black (parts by weight)	50	50	50	50	50	55	10	50	50	50	50
Silane coupling agent (parts by weight)	0.1	0.2	0.3	0.4	2	-	8	0.05	0.5	0	0.2
Clay Clay A (parts by weight)	-	-	-	-	30	-	80	-	-	30	
Clay B (parts by weight)	10	20	30	40	-	-	-	5	50	-	-
Clay C (parts by weight)	-	-	-	-	-	-	-	-			
Clay content (wt%)	17	29	38	44	38	-	89	9	50	38	29
Evaluation Performance on ice	96	92	90	88	92	100	86	100	87	95	102
Failure characteristics	97	94	89	81	92	100	54	99	70	80	85
Angle of contact	102	105	108	110	103	100	116	100	113	10 4	98

Evaluation Results:

As can be seen from Table 2, rubber compositions in which clay A or clay B each having an oil absorption amount within the range of the present invention were blended by more than 10 parts by weight (Examples and Comparative Examples 2, 4, 5) had excellent performance on ice as compared to a rubber composition in which the clay was not used at all (Comparative Example 1) of the clay blended only with an insufficient amount (Comparative Example), or, a rubber composition in which the clay C blended therewith had an oil absorption amount out of the range of the present invention (Comparative Example 6). On the other hand, the failure characteristics tend to be deteriorated by the blend of the clay. The deterioration of the failure characteristics could be kept within a practically allowable range at the blending amount of the clay of less than 40 parts by weight (Examples), whereas the failed characteristics were reduced excessively in the rubber composition at the blending amount of the clay of more than 40 parts by weight (Comparative Examples 2, 4). Particularly, if the blending amount of the carbon black as the reinforcing agent was insufficient, deterioration of the failure characteristics was inevitable even if a great amount of silane coupling agent was blended (Comparative Example 2). Further, even if a clay having the oil absorption amount within the range of the present invention was blended by an amount within the range of the present invention, if the silane coupling agent was not blended in the rubber composition (Comparative Example 5), a problem resulted in the failure characteristics from a practical point of view. Accordingly, the performance on ice can be improved while keeping the failure characteristics within a practically allowable range by blending a clay having the oil absorption amount within the predetermined range in an amount within the predetermined range. Further, it can be seen that blend of the carbon black by more than 50% by weight is preferred for ensuring failure characteristics with safety.

Further, it can be seen from comparison between Example 3 and Example 5 that the performance on ice can be improved more by blending with silane coupling agent not alone by pre-treating the clay with silane.

Further, it can be seen in Example 1 - 5 that the angle of contact is increased in proportion with the blending amount of the clay treated with the silane coupling agent to improve the performance on ice. It can thus be seen that the silane coupling agent bonded with the clay by previously treating the clay acts on the hydrophilic portion in the rubber composition together with the clay to effectively improve the water repellency of the tread rubber. Furthermore, it can also be seen from comparison between Example 5 and Comparative Example 5 that blending of the silane coupling agent contributes not only to the improvement of the failure characteristics together with the clay but also to the improvement of the performance on ice by the synergistic effect with the clay.

Claims

1. A tread rubber composition comprising a diene rubber comprising at least one rubber selected from the group consisting of natural rubber, polyisoprene and polybutadiene as a main ingredient and, based on 100 parts by weight of said diene rubber, characterised by from 10 to 40 parts by weight of a clay comprising kaolinite as a main ingredient and having an oil absorption amount of from 50 to 70g/100g and from 0.1 to 8 parts by weight of a silane coupling agent.

2. A tread rubber composition according to claim 1, characterised in that the silane coupling agent is incorporated in the clay prior to mixing the rubber composition.

3. A tread rubber composition according to claim 1 or 2, characterised in that the clay is sintered at a temperature from 600 to 800°C.

4. A tread rubber composition according to claim 3, characterised in that the clay is amorphous meta-kaolin.

5. A tread rubber composition according to any of claims 1 to 4, characterised by 50 to 90 parts by weight of a reinforcing agent.

6. A tread rubber composition according to claim 5, characterised in that at least one material selected from the group consisting of carbon black and silica is used as the reinforcing agent.

7. A tread rubber composition according to any of claims 1 to 6, characterised in that the silane coupling agent used is represented by the formula: X_3SiR in which X represents an alkoxy group or a chlorine atom, R represents one of vinyl, glycide, methacryl, amino, mercapto, epoxy and imide groups, or represented by the formula:

$$(C_nH_{2n+1})_3\text{-Si-}(CH_2)_m\text{-}S_k\text{-}(CH_2)_m\text{Si-}(C_nH_{2n+1}0)_3$$

in which n represents an integer of 1 to 4, and m and k each represents an integer of 1 to 8.

8. A tyre characterised by a tread comprising the tread rubber composition of any of claims 1 to 7.

FIG. 1

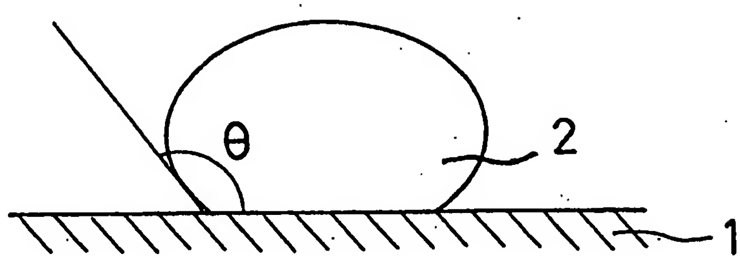
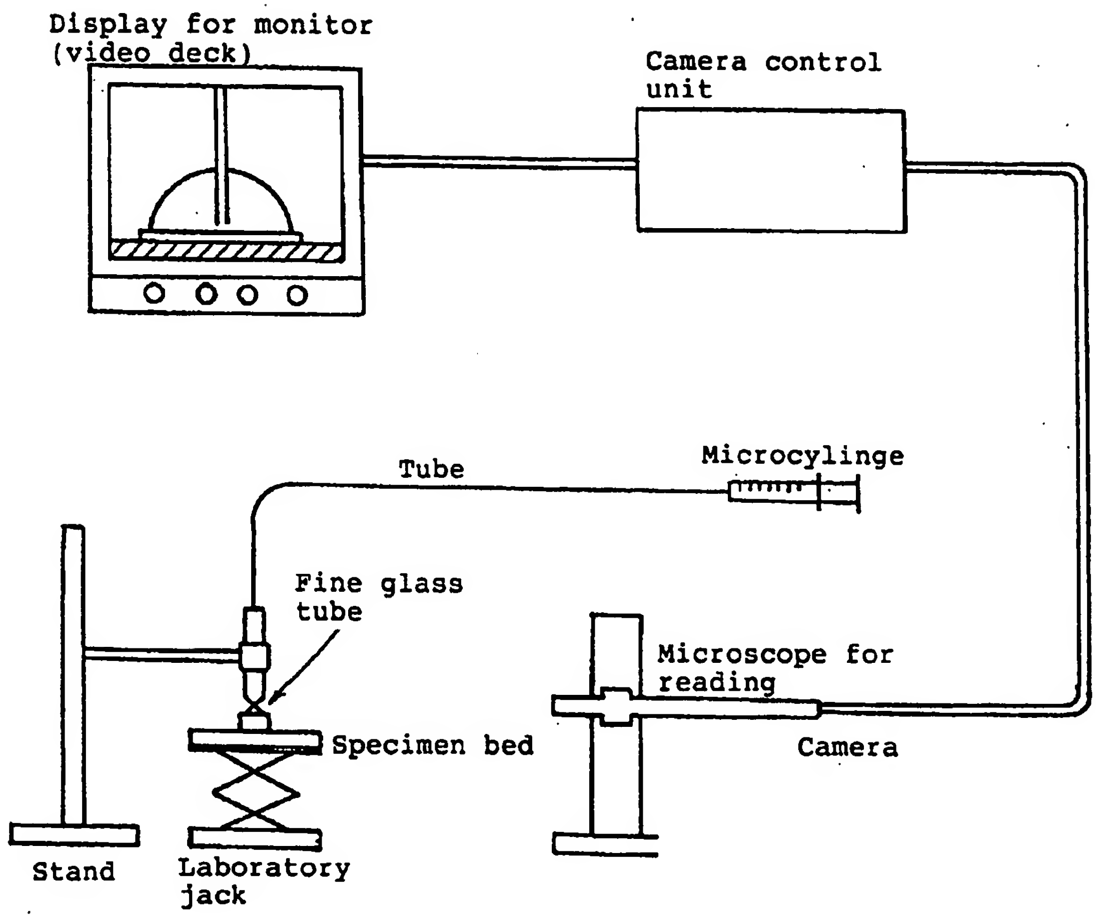


FIG. 2


Display for monitor
(video deck)
Camera control
unit
Microcylinge
Tube
Fine glass
tube
Microscope for
reading
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